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(54) Refractory Coatings

(57) A method for "hot end" coating of vitreous articles, comprises forming refractory magnesium oxide coatings from aqueous solutions of magnesium nitrate, acetate or formate which are applied to the vitreous surface at an elevated temperature to evaporate the

water from the solution and pyrolytically decompose magnesium compound to form a transparent magnesium oxide coating. A lubricious coating comprising at least one of waxy polyolefins, beeswax, fatty acids or alkali metal salts thereof, or polyvinyl alcohol may be applied to the coating.

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SPECIFICATION

Process for Coating Vitreous Article, and Such Coated Articles

The present invention relates generally to refractory "hot end" coatings for vitreous articles such as glassware, and more particularly to improved methods for forming magnesium oxide "hot end" coatings upon glassware from aqueous solutions, and to articles so coated.

The desirability of forming refractory coatings on vitreous surfaces, such as glass, and particularly upon glassware such as bottles, is well known. Pristine glass is theoretically and extremely strong substance. However, when, for example, glassware is subjected to high speed processing machines and normal use in which glass is caused to rub against glass, scratches, abrasions, and other physical damage rapidly degrades the surface of the glass thereby providing sites for initiation of failure throughout the glass. Also, glass is subject to attack by various atmospheric constituents, particularly moisture. Accordingly, it has been an accepted practice in the production of glassware to form a refractory, so-called "hot-end" coating upon the newly formed glass, usually at or before the annealing lehr while the glassware is at an elevated temperature. After formation of a refractory "hot end" coating, it is conventional practice to thereafter apply a lubricious "cold end" coating at lower temperatures. "Cold end" coatings conventionally include, for instance, waxy polyethylene, fatty acids, beeswax, and other such lubricious compositions, either alone or in combination.

The "hot end" coatings, to which the present invention pertains, display particular requirements which distinguish "hot end" coatings from a number of other coatings previously employed upon glass for various purposes. For instance, thick coatings of tin oxide and magnesia have been applied to, for instance, electrical insulators. Other thick coatings of tin oxide have been applied to provide electrical conductivity for defrosting of glass surfaces by employing the tin oxide coating as a resistance element. Semi-transparent, colored coatings have been utilized for decorative purposes and, in some instances, for tinting of glass.

"Hot end" coatings have a number of requirements not met by many known glass coatings. Typically, such coatings should be non-toxic as a coating, and also are desirably formed from compositions which are not in themselves toxic and which do not form toxic byproducts. The coatings formed should not change the appearance of the glassware, i.e., are colorless and substantially free of iridescence. Torque requirements of closures should not be altered.

Since glassware is formed at high rates, coatings must be conveniently applied and utilize relatively economical solvents and compounds. Further, "hot end" coatings must be resistant to normal handling and processing, such as washing, and

must tenaciously adhere to the glass to provide a suitable base for lubricious "cold end" coating. Contrary to the purpose of certain other glass coatings, "hot end" coatings should have high electrical resistance to avoid galvanic action between, for instance, container closures and other materials which come in contact with the glass under damp conditions. The "hot end" coating itself should not function as an electrolyte in contact with metal closures. Thus, it will be recognized that "hot end" coatings or glassware are a well recognized group of materials having characteristics and requirements distinct from other glass coatings.

Currently, "hot end" coatings are generally tin oxide or titanium oxide, formed from vapors of anhydrous tin or titanium tetrachloride or from aqueous solutions of such compounds. However, previously "hot end" coatings of tin, titanium or zirconium oxide have also been formed from organic compounds applied in or from organic solutions.

A number of prior art discussions exist concerning the various coatings. For instance, U.S. Letters Patent 2,165,819, issued July 11, 1939, discloses an electrical insulator of magnesium titanate suitable for formation on ceramic substances such as condensers. Magnesium titanate is disclosed as being suitable for a narrow, and quite specific coating purpose, but does not correlate with the requirements of a "hot end" coating.

U.S. Letters Patent 3,323,889, issued June 6, 1967, discloses a coating system for the purposes of the instant invention, but involves the use of zirconium and titanium oxide as a "hot end" coating applied from an organic solvent solution in conjunction with relatively conventional "cold end" coatings. Many organic solvents are expensive, often flammable, and cause objectionable pollution of the atmosphere. However, U.S. Letters Patent 3,323,889 is pertinent in setting forth many of the requirements of a "hot end" coating.

U.S. Letters Patent 3,450,574, issued June 17, 1969, is concerned with the preparation of a magnesia coating on refractory bodies. Preferably, the patent teaches the formation of a thin film of metal under reducing conditions and thereafter providing oxidizing conditions to form the oxide.

Sintering techniques are also disclosed.

U.S. Letters Patent 3,516,811, issued June 23, 1970, primarily discloses apparatus for applying "hot end" coatings in laminar flow condition, but also contains a fairly comprehensive listing of various prior art patents dealing with "hot end" end "cold end" coatings.

Typical of the hot end coatings discussed by U.S. Letters Patent 3,516,811 is U.S. Letters Patent 3,561,940, issued February 9, 1971, which concerns the formation of tin oxide coatings by the pyrolytic composition of anhydrous stannic tetrachloride vapors in a moisture-free carrier gas. While tin oxide is a desirable and workable "hot end" coating, the by-

products of the pyrolytic decomposition include hydrochloric acid (upon hydrolysis with atmospheric moisture) which presents serious problems with regard to attack of surrounding equipment and pollution of the atmosphere. Such installations may require expensive scrubbing equipment to remove the unused stannic tetrachloric and hydrochloric acid from the exhaust gases.

10 U.S. Letters Patent 3,694,299, issued September 26, 1972, discloses a means for fusing glass sheets together utilizing an organo-metallic film forming solution in which the metallic constituent may include magnesium.

15 However, the solution utilizes volatile and combustible solvents as well as resins which would be entirely inappropriate for use in a "hot end" coating composition for the reasons discussed above.

20 U.S. Letters Patent 3,711,322, issued January 16, 1973, discloses organic solvent based compositions utilizing two metal compounds, one of which may be a magnesium compound such as magnesium acetate, to form semi-transparent, colored metal oxide coatings. For numerous reasons including transparency, color, organic solvents, etc., such coatings would not be useful as "hot end" coatings.

25 U.S. Letters Patent 3,847,583, issued November 12, 1974, similarly discloses the use of two metal compounds dissolved in an organic solvent to form coatings. Titanium oxide and, it is believed, tin oxide, are discussed, and specific mention is made that alkali or alkali earth oxides are not operable to form pyrolytically induced oxide coatings.

30 U.S. Letters Patent 3,926,103, issued December 16, 1975, discloses a recovery system for a spray solutions of tin compounds.

35 Finally, U.S. Letters Patent 3,984,591, issued October 5, 1976, discloses the formation of metallic oxide coatings from metallic salts utilizing, as a critical feature of the invention, aprotic solvents of specific dipolar moments which would be inappropriate for "hot end" coatings. Mention is made of spraying aqueous solutions, but such coatings are characterized as being readily removed in the form of dust by passing a finger over the coating.

40 Thus, on the basis of the above prior art, the only workable "hot end" coatings are those involving pyrolytic decomposition from objectionable organic solvents or from halides. In both cases, objectionable by-products in the form of exhaust fumes are presented. The better, more economical coatings involve pyrolytic decomposition of stannic tetrachloride with the resulting formation of hydrochloric acid.

45 The present invention, which provides a heretofore unrecognized and unavailable improvement over previous methods for forming "hot end" coatings on glassware, involves pyrolytic decomposition of solutions of water soluble magnesium compounds which, directly or

50 indirectly, form magnesium oxide containing

55 coating upon glassware heated above about 450°C, preferably between 500—700°C. Particularly, magnesium acetate, which provides high quality coatings with innocuous by-products, and also magnesium nitrate which forms a desirable coating with less desirable by-products are preferred, though other magnesium compounds have also been found to be operable if sufficiently water soluble.

60 Accordingly, advantage of the present invention is to provide a new and improved coating method and refractory coating for glassware which adheres strongly to the glassware and does not substantially alter the

65 appearance of the glassware.

70 Another advantage of the present invention is to provide a new and improved coating method and coating for glassware which displays an affinity for "cold end" coatings and provides both wet and dry lubrication with such "cold end" coatings.

75 Still another advantage of the present invention is to provide a new and improved coating method and improved coating for

80 glassware which coating is non-toxic.

85 These and other advantages of the present invention will be apparent from the following description of the invention.

90 According to the present invention, "hot end" coatings of magnesium oxide are formed on vitreous substances such as glassware by applying an aqueous solution of magnesium compounds having specific properties to glassware heated to an elevated temperature, i.e.,

95 above 400°C to 450°C, and preferably above about 550°C. Typically, such surfaces are not heated above 700°C, but in specific instances may be heated to higher temperatures without adversely affecting the coating in accord with the

100 instant invention. The limiting upper temperature depends upon the substrate and the coating and the lower temperature depends upon the coating.

105 Many of the advantages of the instant invention accrue from the use of aqueous solutions of the magnesium compounds. Essentially, the compounds must be water soluble magnesium compounds. The magnesium compounds are dissolved in a water carrier and are sprayed upon the hot glassware preferably in the form of a mist

110 or fine spray of the solution. It is also important that the magnesium compound decompose to magnesium oxide at the temperatures existing on the surface of the glassware and, preferably, after initially melting as the dissolved magnesium

115 compound.

120 While the mechanism is not entirely understood, it is postulated that the magnesium compound is deposited as a solid upon the heated glassware as the solvent is evaporated from the

125 solution. The magnesium compounds initially melt and then pyrolytically decompose to form magnesium oxide. Accordingly, if the original magnesium compound, or any magnesium compound other than magnesium oxide formed

130 during the course of pyrolytic decomposition is

stable at the temperature involved, satisfactory results will not be obtained. For instance, most magnesium compounds which are water soluble and include sulfur, i.e. magnesium sulfate

5 heptahydrate $MgSO_4 \cdot 7H_2O$, and other such magnesium compounds including sulfur, i.e., magnesium thiosulfate $MgS_2O_3 \cdot 6H_2O$, magnesium sulphite $MgSO_3 \cdot 6H_2O$ which form, upon initial decomposition, magnesium sulfate

10 $MgSO_4$ (decomposition temperature of about $1124^\circ C$) are not workable. This temperature is above that to which glassware can conventionally be heated. Thus the final coating is magnesium sulfate rather than magnesium oxide and does not

15 display desirable "hot end" coating characteristics. However, such sulfur containing compounds would be expected to provide good results in some instances at higher temperatures with, for instance, ceramics.

20 Examples of magnesium compounds which meet the above criteria and form worthwhile "hot end" coatings include magnesium acetate, magnesium nitrate, and magnesium formate. As mentioned earlier, the sulfur containing

25 compounds generally are not decomposable to magnesium oxide under the available temperatures.

Other magnesium compounds such as magnesium benzoate $Mg(C_7H_5O_2)_2 \cdot 3H_2O$,

30 magnesium lactate $Mg(C_6H_5O_7) \cdot 3H_2O$, magnesium citrate $Mg(C_6H_5O_7) \cdot 5H_2O$ and magnesium dicitrate $Mg_2(C_6H_5O_7) \cdot 5H_2O$ appear to be too insoluble to provide clear, adherent coatings. While coatings are formed, the coatings

35 tend to be cloudy and water soluble. This appears to be a function of the solubility of the magnesium compound. Highly soluble magnesium compounds, as discussed above, are believed to form small particles of the compound upon the

40 glassware which particles are believed to immediately melt into a smooth continuous layer of the compound, and then pyrolytically decompose into magnesium oxide. Water insoluble or marginally soluble magnesium

45 compounds do not yield the desired results, possibly because of the formation of solid magnesium compound particles in the presence of substantial quantities of solvent which do not melt into a smooth layer prior to pyrolytic

50 decomposition.

Of the magnesium compounds which satisfy the basic criteria, i.e., high water solubility, melting point below the general surface temperature of heated glass, and pyrolytic

55 decomposition into magnesium oxide at the surface temperature of the glass, magnesium acetate is a particularly preferred composition having properties significantly superior to those of other of the operable magnesium compounds. For

60 instance, magnesium acetate is highly soluble in water, generally employed at between 10 parts by weight of water to one part by weight of magnesium acetate to one part by weight of water to one part by weight of magnesium acetate, and typically at five parts by weight of

65 water to one part by weight of magnesium acetate, and melts at $80^\circ C$ and decomposes at $323^\circ C$, presumably into magnesium oxide. Upon decomposition, magnesium acetate forms water and carbon dioxide as by-products. Magnesium oxide, magnesium acetate and the byproducts are all non-toxic and non-corrosive materials.

70 Operably magnesium oxide formed by applying magnesium acetate in an aqueous solution to reheated glassware may be produced at surface temperatures above about $400^\circ C$ to $450^\circ C$. However, the preferred range is between $680^\circ C$ to $700^\circ C$. Below about 550° to 600° , the transparency of the coating become somewhat

75 uneven. Above about $680^\circ C$ to $700^\circ C$, the "hot end" coating lubrication qualities diminish somewhat, particularly when wet. With newly formed glassware with internal temperatures higher than the surface temperature, lower initial

80 temperature may be operable.

85 Magnesium nitrate forms excellent coatings from aqueous solutions, but forms NO_x by-products upon pyrolytic decomposition. However, magnesium nitrate melts at $89^\circ C$ and

90 decomposes at $330^\circ C$ yielding excellent coatings at normal "hot end" glass coating temperatures.

95 The resulting magnesium oxide "hot end" coatings in accord with the instant invention should, of course, be thick enough to afford substantial protection to the protected vitreous surface, such as glassware. However, in most instances, the coating should not be thicker than about one wavelength of light to which it is typically exposed, i.e., about one micron, to avoid wave

100 interference within the coating leading to iridescence. In some instances, coatings may be thicker without otherwise degrading the results. Iridescence, at times, is considered a desirable appearance. Also, thicker coatings tend to be

105 more electrically conductive. As a rule, the coating thickness may be easily controlled by regulating the exposure time of the heated glassware to a given concentration of the magnesium compound aqueous solution.

110 As discussed above the magnesium compound should be applied to a reheated surface at at least about $400^\circ C$, preferably between $550^\circ C$ and $700^\circ C$, though higher temperatures are suitable for coating purposes. In most instances though,

115 the vitreous surface may be adversely affected by higher temperatures, though certain vitreous surfaces, such as ceramic, may be heated to quite elevated temperatures. Somewhat lower temperatures may be employed with newly

120 formed glass. Each magnesium compound suitable for forming magnesium oxide coatings in accord with the instant invention of course display differing melting points and pyrolytic decomposition points. Accordingly, optimum temperatures may vary somewhat from compound to compound, though the above specified temperatures are generally operable. For instance, magnesium acetate is preferably applied to reheated surfaces between $680^\circ C$ and $700^\circ C$,

though good results may be obtained outside of this range.

The concentration of the magnesium compound in aqueous solution is not critical. Of course, more dilute solutions require evaporation of greater quantities of water and accordingly cool the glassware surface more. As a rule, between about 10% to 50% by weight of magnesium compound to weight of solution has been found to be a desirable operating range, though not a critical range. Preferably about midpoint of this range is employed.

It should be noted that the solubility of the magnesium compound in water is an independent consideration from that of the actual concentration of the magnesium compounds in solution when applied to vitreous surfaces. Thus, compounds which marginally dissolve at the above-specified concentration are not necessarily desirable coating compounds. As the water evaporates, solid particles of the magnesium compound is of course formed on the vitreous surface. This result can be prematurely accomplished in near saturated solutions of magnesium compounds. Accordingly, while not firmly established, it is believed that the more highly soluble magnesium compounds operable in the instant invention do not form solid particles until but small amounts of water remain thereby minimizing the concurrent existence of solid matter and solution and leading to melting of the particles to form an initial coating.

It is contemplated that the magnesium oxide coatings formed in accordance with the instant invention will be further coated with lubricious "cold end" coatings as are well known in the art. Generally, this is accomplished by spraying the lubricious coatings, usually as aqueous solutions, onto the vitreous surfaces after, in the case of glassware, annealing is substantially complete. Vapors of organic lubricious materials may also be employed to accomplish the coating. "Cold end" coatings are well known in the art. Typically such coatings include one or more lubricious constituents such as waxy polyolefins such as polyethylene having a molecular weight between 1000 and 2000, fatty acids such as oleic, palmitic, stearic, lauric, or mixtures thereof, alkali metal salts of fatty acids, beeswax and polyvinyl alcohol. Such "cold end" coatings are well known in the art and are applicable to the magnesium oxide coatings in accord with the instant invention.

A more detailed appreciation of the invention will be gained from the following examples.

Example 1

An aqueous solution of magnesium acetate tetrahydrate was prepared by adding one part by weight of the magnesium acetate compound to five parts by weight of water. A glassware article (bottle) was heated to provide a surface temperature of about 640°C. The solution of magnesium acetate was sprayed at a flow rate of about .5 grams per second while the glassware

65 was rotated upon a turntable at 78 rpm. Approximately 16 revolutions of the glassware bottle occurred during an application. A clear, transparent coating of magnesium oxide was formed on the bottle. Thereafter, when the 70 glassware had cooled to 120°C, a commercial "cold end" coating, i.e. Glas-Lube 1000 available from Crown Chemical Company, diluted by a factor of 100 by weight in distilled water was sprayed at the rate of 1 gram of "cold end" 75 coating solution per second for a period of 5 revolutions of the glassware on the turntable as discussed above. The thus coated article with both "hot end" and "cold end" coatings was tested for lubrication both wet and dry. Under 80 both conditions lubrication was found to be excellent when two such glassware articles were manually rubbed together.

Example 2

A glassware article was coated utilizing the same techniques and compositions as in Example 1 with the exception that the article was passed through a coating hood at a rate of about .8 feet per second while the aqueous solution of magnesium acetate was sprayed onto the article 90 through four nozzles arranged to provide uniform coverage of the bottle on one pass through the coated hood. Results substantially identical to those of Example 1 were obtained. Numerous other similar examples of coating of magnesium 95 acetate were carried out with the following observations; excellent coatings were observed utilizing between about 10% by weight (actually 9.1%) of magnesium acetate to water to 50% by weight of magnesium acetate to water; technical 100 grades of magnesium acetate and ordinary tap water were found to be entirely workable; and a preferred range of 550°C to 700°C was established, and a particularly preferred range being 680°C to 700°C was noted, for reheated 105 glass with the lubrication degrading somewhat, particularly when wet at higher temperatures, and the appearance of the coating degraded somewhat at lower temperatures.

Example 3

110 4.1 parts by weight of water and 1 part by weight of magnesium nitrate hexahydrate were mixed to provide a solution of magnesium nitrate. The thus prepared solution of aqueous magnesium nitrate was applied to a glassware 115 article utilizing substantially identical conditions as those employed in Example 1. The resulting "hot end" coating was transparent and attractive in appearance, and the article after "cold end" coating provided good lubrication both dry and 120 wet when tested in a manner identical to that utilized in Example 1.

Other tests with magnesium nitrate were conducted with coating results substantially equal to those obtained with magnesium acetate, 125 though lubrication qualities were poorer utilizing more dilute solutions, and were marginal at about

10% by weight and below of magnesium nitrate to water solutions.

Example 4

4.4 parts by weight of water and 1 part by weight of magnesium formate were mixed to form an aqueous solution of magnesium formate. The thus formed aqueous solution of magnesium formate was applied to a glassware article heated to a temperature of about 660°C to 680°C as described in Example 1. An attractive transparent coating was formed. "Cold end" coating was applied as described in Example 1 and the article tested for lubricity. Lubricity was found to be good when dry and fair wet. In general, magnesium formate was found to be an acceptable and desirable "hot end" coating material.

Example 5

Ten parts by weight of water and 1 part by weight of magnesium sulfate were mixed to form a magnesium sulfate aqueous solution. The thus formed aqueous solution of magnesium sulfate was applied to a glassware article heated to about 720°C and the article was otherwise treated and coated as described in Example 1. The "hot end" coating was spotty, the article, including additional "cold end" coating, displayed poor lubricity. It is believed that magnesium sulfate formed the coating. Thus, at the temperatures normally employed with glassware, magnesium sulfate was found to be unsatisfactory as having a decomposition point (about 1124°C) above that of the working range of most glassware.

Example 6

3.3 parts by weight of water was mixed with 1 part by weight of magnesium benzoate. The magnesium benzoate did not entirely dissolve in the water. The magnesium benzoate solution formed, which was more dilute than the initial constituents, was decanted and applied to a glassware article heated to a temperature of about 640°C in the manner described in Example 1. The resulting "hot end" coating was cloudy. After applying a "cold end" coating as described in Example 1, the article was tested for lubricity. The results were poor because of poor adhesion of the "hot end" coating. It was found that the "hot end" coating would wash off in water. It is believed that magnesium benzoate is not sufficiently soluble to form a clear, adherent coating as required of the magnesium compound in accord with the instant invention. Similar results were obtained with magnesium lactate, magnesium citrate, and magnesium dicitrate, all of which required decanting utilizing similar amounts of water and magnesium compounds.

From the above description, it will be apparent that the instant invention discloses an advantageous means for providing "hot end" coatings upon glassware. Aqueous coating solutions of magnesium compounds are much easier to utilize and yield less troublesome by-products than the anhydrous compounds

previously employed in many instances. Further, one skilled in the art can, with little effort, identify

65 magnesium compounds suitable for use in the instant invention. Such compounds are highly soluble in water, i.e., form solutions of at least 50% by weight, and preferably much higher, of the magnesium compound in water, display
 70 melting point below that of the surface to be coated and pyrolytic decomposition point to magnesium oxide below the temperature of the surface to be coated but above the melting point of the magnesium compounds. Actual testing is
 75 easily accomplished by substituting various solutions in a coating hood.

In operation, it is preferred to conduct the vitreous articles, and particularly newly formed glassware, through a coating hood in which the aqueous solution of magnesium compound is applied to the bottle as a fine mist or spray. Surface temperatures of the glassware and concentration of the aqueous magnesium solution are not critical within broad limits but do generally
 85 influence the nature of the "hot end" coating. Highly dilute solutions, of course, may cause objectionable cooling of the unannealed articles.

Although only several specific examples and embodiments of the present invention have been
 90 presented in detail, those skilled in the art will recognize numerous changes and modifications within the scope of the invention. Such changes may be made without departing from the scope of the invention, as defined by the following claims.

95 Claims

1. A vitreous article having protective and lubricious coatings thereon, characterized in that the protective coating is a transparent, refractory coating comprising magnesium oxide adhered

100 directly to the surface of the vitreous article.
 2. A coated vitreous article as set forth in Claim 1 characterized in that the lubricious coating includes at least one constituent selected from the group consisting of waxy polyolefins,
 105 beeswax, fatty acids, alkali metal salts of fatty acids, and polyvinyl alcohols.

3. A coated vitreous article as set forth in either of Claims 1 and 2 characterized in that the magnesium oxide refractory coating is between .1
 110 micron and 1 micron thick.

4. A method for forming protective, refractory coatings upon vitreous articles characterized in that a vitreous article heated to an elevated temperature is positioned within a coating

115 location, a solution of a magnesium compound is applied upon the surface of the heated vitreous article, the solvent from the magnesium compound solution is evaporated at the surface of the vitreous article, and the magnesium

120 compound is pyrolytically decomposed at the surface of the vitreous article to form a continuous, adherent and substantially transparent, refractory coating comprising magnesium oxide upon the surface of the vitreous article.

5. A method for coating vitreous articles as set

forth in Claim 4 characterized in that the solution of magnesium compound is an aqueous solution.

6. A method for coating vitreous articles as set forth in either of Claims 4 or 5 characterized in

5 that the surface of the article is at a temperature above 400°C.

7. A method for coating vitreous articles as set forth in any of Claims 4, 5, and 6, characterized in that the surface of the vitreous article is at a

10 temperature between 400°C and 700°C.

8. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6 and 7 characterized in that the magnesium compound is melted after the solvent is substantially evaporated to form a

15 coating of magnesium compound upon the vitreous article surface, and thereafter is pyrolyzed to form the coating of magnesium oxide.

9. A method for coating vitreous articles as set

20 forth in any of Claims 4, 5, 6, 7 and 8 characterized in that the solution of magnesium compound is spread upon the surface of vitreous article in the form of a mist.

10. A method for coating vitreous articles as

25 set forth in any of Claims 4, 5, 6, 7, 8 and 9 characterized in that the magnesium compound is highly soluble in water, has a melting point below the surface temperature of the vitreous article, and a pyrolytic decomposition point below the

30 surface temperature of the vitreous article and above the melting point of the magnesium compound.

11. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7, 8, 9 and 10

35 characterized in that the magnesium compound is selected from the group consisting of magnesium acetate, magnesium nitrate and magnesium formate.

12. A method for coating vitreous articles as

40 set forth in any of Claims 4, 5, 6, 7, 8, 9, 10 and 11 characterized in that the magnesium compound is magnesium acetate.

13. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7, 8, 9, 10, 11,

45 and 12 characterized in that the magnesium acetate is applied as a solution comprising between 10% and 50% by weight of magnesium acetate relative to the solvent.

14. A method for coating vitreous articles as

50 set forth in any of Claims 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13 characterized in which the magnesium refractory coating is between about .1 micron and 1 micron thick.

15. A method for coating vitreous articles as

55 set forth in any of Claims 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14 characterized in that the vitreous article is cooled after formation of the magnesium oxide coating and a second lubricious coating is applied thereto at a lower temperature.

60 16. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15 characterized in that a lubricious coating including at least one compound from the group consisting of waxy

65 polyolefins, beeswax, fatty acids, alkali metal salts of fatty acids, and polyvinyl alcohols is applied to the magnesium refractory coating.